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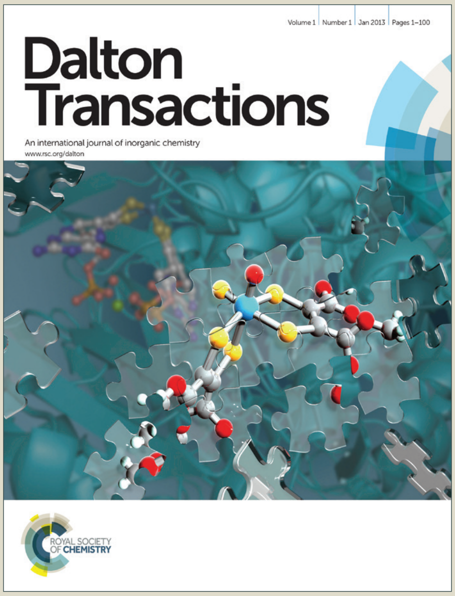

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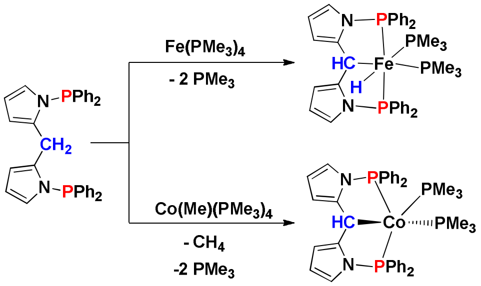
A new PC(sp^3)P ligand and its pincer complexes of Fe and Co are reported.



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COMMUNICATION

A new PC(sp^3)P ligand and its coordination chemistry with low-valent iron, cobalt and nickel complexes†

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Gengyu Zhu, Xiaoyan Li, Guoqiang Xu, Lin Wang, Hongjian Sun*

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A new PC(sp^3)P ligand *N,N'*-bis(diphenylphosphino)dipyrromethane [PCH_2P] (1) was prepared and its iron, cobalt and nickel chemistry explored. Two pincer-type complexes [PCHP]Fe(H)($(PMe_3)_2$) (2) and [PCHP]Co($(PMe_3)_2$) (4) were synthesized in the reaction of 1 with Fe($(PMe_3)_4$) and Co(Me)($(PMe_3)_4$). 1 reacted with Co($(PMe_3)_4$) and Ni($(PMe_3)_4$) to afford Co(0) and Ni(0) complexes [PCH_2P]Co($(PMe_3)_2$) (3) and [PCH_2P]Ni($(PMe_3)_2$) (5). The structures of complexes 2-5 were determined by X-ray diffraction.

The "pincer era" began from the initial investigations of PCP ligands by Shaw[1] in the late 1970s. However, exploration of the PC(sp^3)P ligands has been overshadowed for quite a long time by their aromatic counterparts.[2] This imbalance originated from not only the greater synthetic convenience for access to diverse ligands, but also the greater thermal and conformational stability of PC(sp^2)P ligands compared to PC(sp^3)P ligands.[3] Nevertheless, more recent work[4] has clearly demonstrated that the sp^3-hybridized carbon coordinated to the metal centre highly influences the reactivity of the pincer complex and many interesting transformations have been spotted.[5] This makes the PC(sp^3)P pincer system more and more attractive for further developments.

So far, the known PC(sp^3)P ligands are relatively limited,[5] and research in this field has mainly been focused on platinum group metals[6-10] and nickel[11] chemistry. Due to our long-standing efforts in the chemistry of iron, cobalt and nickel,[12] we have set out to study the activation of C(sp^3)-H bond in pincer ligands by these metals. Several PC(sp^3)P pincer complexes of iron and cobalt were reported in our previous work,[12a] but the examples of this type are still very limited. Among all the known PC(sp^3)P ligands, a particular one based on a dipyrromethane (DPM) scaffold pioneered by Ozerov and coworkers[6b] has caught out interest for two reasons (**Fig. 1**).

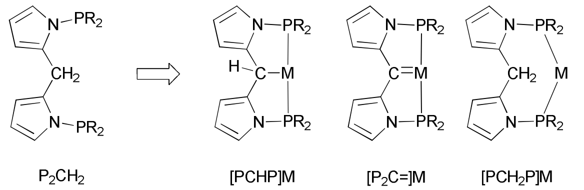
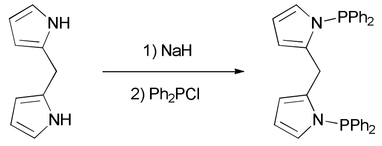


Fig. 1 DPM-based PC(sp^3)P ligand and its coordination patterns.

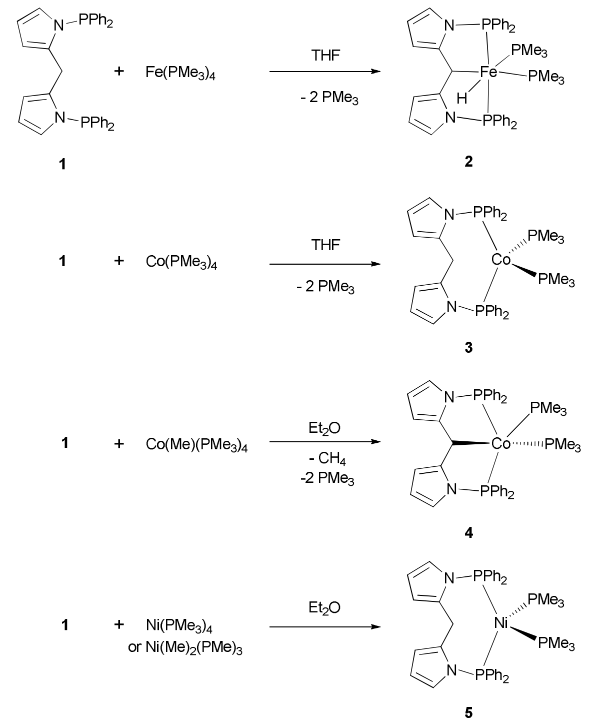


PCH_2P (**1**)

Scheme 1 Synthesis of the ligand [PCH_2P].

First, its construction is very straightforward, by taking advantage of the facile N-P bond formation. More important, the pyrrole ring as a rigid linker makes the communication between the metal centre and the C(sp^3)-H bond more efficient, which increases the chance for cyclometalation.[6b,8b] However, since the initial studies no further exploration has been made to this type of PC(sp^3)P ligand because C(sp^3)-H cleavage is a challenge. Herein, we report a new DPM-based PC(sp^3)P ligand and its first pincer complexes with iron and cobalt. We also describe the formation of its cobalt(0) and nickel(0) complexes where it was utilized as a bidentate ligand.

The new ligand *N,N'*-bis(diphenylphosphino)dipyrromethane [PCH_2P] (**1**) was prepared according to a slightly modified procedure[6b] developed by Ozerov for the original ligand P_2CH_2 (**Scheme 1**). Reaction of 2 equiv of Ph_2PCl with deprotonated dipyrromethane in THF afforded compound **1** which was isolated as a colourless viscous oil in 62% yield by column chromatography on silica gel under N_2. **1** was characterized by ^1H, ^{31}P, and ^{13}C NMR in solution. It displayed one singlet



Scheme 2 Preparation of complexes **2** – **5**.

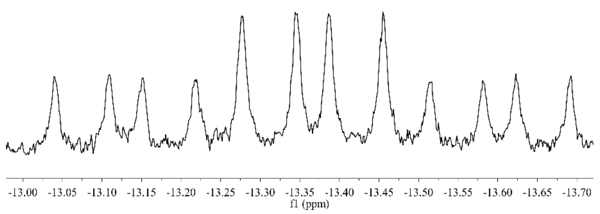


Fig. 2 Hydride resonance of complex **2**

resonance at δ 35.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The protons of the CH_2 linkage resonate at δ 4.81 ppm as a singlet in the ^1H NMR spectrum, and the carbon of the CH_2 linkage resonates at δ 25.4 ppm as a triplet with J_{CP} = 18 Hz in the ^{13}C NMR spectrum.

We investigated its coordination chemistry with iron, cobalt and nickel (**Scheme 2**). When **1** was treated with 1 equiv of $Fe(PMe_3)_4$ in THF, the solution turned dark brown after 24 h. Complex [PCHP]Fe(H)$(PMe_3)_2$ (**2**) was isolated as golden yellow needles from diethyl ether. A typical ν(Fe-H) stretching band was found at 1922 cm^{-1} in the IR spectrum. The characteristic hydride signal of **2** in the ^1H NMR spectrum (**Fig. 2**) as a tdd peak was found at -13.36 ppm with J_{PH} coupling constants of 71.1, 32.7 and 20.7 Hz. A single crystal X-ray structure analysis of **2** established the structural details associated with the coordination of the new PC(sp^3)P ligand. In the molecular structure of **2** (**Fig. 3**), iron is centred in a distorted octahedral geometry. The axial angle P1-Fe1-P2 is 148.40(6)°, greatly deviating from 180°. [C29Fe1P3P4H1] are in the equatorial plane. The Fe1-C29 distance (2.166(5) Å) is within the range of Fe-C(sp^3) bonds.[13] Both Fe-P4 distance (2.264(2) Å) and Fe-P3 distance (2.240(2) Å) are longer than Fe1-P1 distance (2.156(2) Å) and Fe1-P2 (2.164(2) Å), presumably due to the strong *trans*-influence of the hydrido H and C(sp^3) atom being greater than that of the phosphorus atoms.

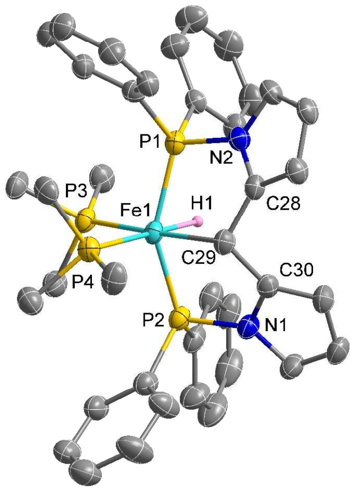


Fig. 3 Molecular structure of complex **2**. The thermal ellipsoids are displayed at 50% probability level, and hydrogen atoms except for Fe-H are omitted for clarity. Selected bond lengths (Å) and angles [°]: Fe1-H1 1.64(6), Fe1-C29 2.166(5), Fe1-P1 2.156(2), Fe1-P2 2.164(2), Fe1-P3 2.240(2), Fe1-P4 2.264(2); C29-Fe1-H1 92(2), C29-Fe1-P3 175.7(2), C29-Fe1-P4 91.3(2), P3-Fe1-H1 84(2), P1-Fe1-P2 148.40(6), P1-Fe1-P3 95.10(6), P1-Fe1-P4 105.65(6), P2-Fe1-P4 102.51(6), P3-Fe1-P4 92.89(6).

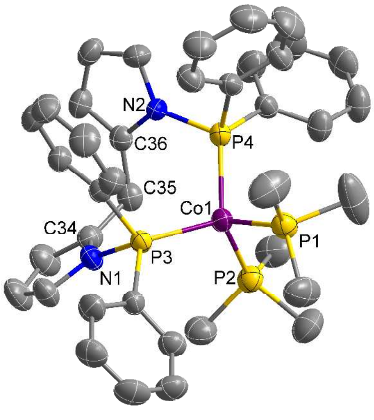


Fig. 4 Molecular structure of complex **3**. The thermal ellipsoids are displayed at 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-P1 2.208(1), Co1-P2 2.235(1), Co1-P3 2.136(1), Co1-P4 2.141(1); P1-Co1-P2 104.87(5), P1-Co1-P3 112.58(5), P1-Co1-P4 105.82(5), P2-Co1-P3 110.35(5), P2-Co1-P4 115.35(5), P3-Co1-P4 107.88(4).

The reaction of **1** with $Co(PMe_3)_4$ was different (**Scheme 2**). After stirring for 24 h in THF at 25 °C, complex [PCH_2P]Co$(PMe_3)_2$ (**3**) was isolated as dark red blocks in the yield of 69%. Complex **3** is a paramagnetic species, and showed no ν(Co-H) stretching band in the IR spectrum, indicating the cleavage of the C(sp^3)-H had not happened. The structure of complex **3** was determined by X-ray diffraction analysis (**Fig. 4**). The cobalt(0) centre is coordinated to two phosphorus atoms of the [PCH_2P] ligand and two PMe_3 molecules. The environment about the cobalt centre is close to

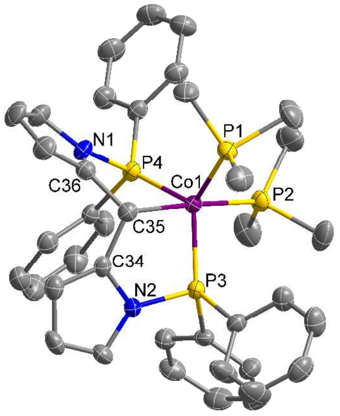


Fig. 5 Molecular structure of complex **4**. The thermal ellipsoids are displayed at 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-C35 2.140(3), Co1-P1 2.2053(9), Co1-P2 2.2119(9), Co1-P3 2.1452(9), Co1-P4 2.1529(8); C35-Co1-P2 176.65(7), P1-Co1-P3 121.59(3), P1-Co1-P4 116.93(3), P3-Co1-P4 117.14(3), C34-C35-C36 109.1(2).

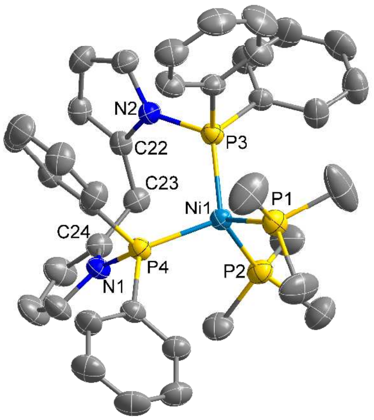


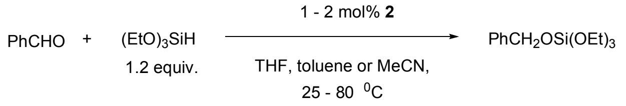
Fig. 6 Molecular structure of complex **5**. The thermal ellipsoids are displayed at 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles [°]: Ni1-P1 2.199(1), Ni1-P2 2.217(1), Ni1-P3 2.149(1), Ni1-P4 2.141(1); P1-Ni1-P2 106.83(4), P1-Ni1-P3 107.35(4), P1-Ni1-P4 111.99(4), P2-Ni1-P3 114.80(4), P2-Ni1-P4 109.68(4), P3-Ni1-P4 111.99(4).

an idealized tetrahedral geometry. The Co1-C35 distance (ca. 3.34 Å) is much longer than those of the known Co-C(sp^3) bonds (2.03-2.15 Å).[14] This suggests no bond interaction exists between these two atoms, thus **1** [PCH$_2$P] only served as a neutral bidentate ligand in this case.

A pincer complex of cobalt bearing this ligand was obtained in the following reaction (**Scheme 2**). Treatment of **1** with an equalmolar amount of $Co(Me)(PMe_3)_4$ in diethyl ether at 25 °C furnished complex $[PCHP]Co(PMe_3)_2$ (**4**) in the yield of 84% as a red powder which can be crystallized in diethyl ether at 0 °C. The existence of the Co-CH moiety in **4** was evidenced by a doublet at δ 3.88 ppm in the ^{1}H NMR spectrum. A pair of doublets at δ 0.76 and 1.06 ppm in the ^{1}H NMR spectrum indicated that the PMe$_3$ ligands are not chemically identical. X-ray crystallography confirmed a slightly distorted trigonal bipyramidal structure of complex **4** (**Fig. 5**). C35 and P2 are *trans*-oriented in the axial positions and the C35-Co1-P2 angle is 176.65(7)°. Two five-membered metallacycles with remarkable ring bending (sum of the internal bond angles is 530.4° and 531.9° respectively) are formed through coordination of the two phosphine arms and the metalated C(sp^3) atom. The Co1-C35 distance of 2.140(3) Å is within the range of Co-C(sp^3) bonds (2.03-2.15 Å).[14]

The reaction of **1** with $Ni(PMe_3)_4$ or $Ni(Me)_2(PMe_3)_3$ afforded the same product $[PCH_2P]Ni(PMe_3)_2$ (**5**) (**Scheme 2**). Complex **5** was isolated as orange crystals in high yield in both reactions. The molecular configuration is depicted in **Fig. 6**. The nickel atom is situated in a distorted tetrahedral coordination sphere. The P1-Ni1-P2 (106.83(4)°), P1-Ni1-P3 (107.35(4)°), P1-Ni1-P4 (111.99(4)°), P2-Ni1-P3 (114.80(4)°), P2-Ni1-P4 (109.68(4)°) and P3-Ni1-P4 (111.99(4)°) angles are all close to 109.5°. The four Ni-P bond lengths of 2.1989(12) Å, 2.2167(11) Å, 2.1490(11) Å, and 2.1408(12) Å are comparable with literature values.[12*c*] Complex **5** can be viewed as a nickel version of Complex **2**. It is noticeable that only $Fe(PMe_3)_4$ formed PC(sp^3)P pincer-type complex with ligand **1** in these three zero valent species ($Fe(PMe_3)_4$, $Co(PMe_3)_4$, $Ni(PMe_3)_4$).

Iron hydride complexes have been playing important roles in many catalytic systems.[15] Recently, several groups, including ours, have been interested in developing iron-catalysed hydrosilylation of aldehydes and ketones.[12c,16] Therefore, we also examined if complex **2** would catalyse similar reactions. Unfortunately, this proved to be unsuccessful although many attempts had been made (**Scheme 3**).



$$PhCHO + \underset{\text{1.2 equiv.}}{(EtO)_3SiH} \xrightarrow[\text{THF, toluene or MeCN, 25 - 80 }^0\text{C}]{\text{1 - 2 mol\% }\mathbf{2}} PhCH_2OSi(OEt)_3$$

Scheme 3 Attempts on the hydrosilylation of benzaldehyde catalyzed by **2**.

In conclusion, a new PC(sp^3)P pincer ligand based on a dipyrromethane backbone was synthesized and its coordination chemistry with iron, cobalt and nickel was investigated. The activation of the C(sp^3)-H bond is strongly metal-depended. Further studies into the coordination chemistry of this ligand and the properties of its resulting complexes are ongoing in our laboratory.

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Notes and references

School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China.

E-mail: hjsun@sdu.edu.cn; Fax: +86 531 88361350.

† Electronic Supplementary Information (ESI) available: Experimental details and characterization of all compounds; crystal structure data for **2**, **3**, **4** and **5**. CCDC 986904–986907. See DOI:

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